BULLETIN

OF THE

BUREAU OF STANDARDS

PRELIMINARY SPECIFICATIONS FOR CLARK AND WESTON STANDARD CELLS.

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Directions for the preparation of materials used in Clark and Weston standard cells, and for their construction, have been published from time to time.[1]

The following specifications are based upon these directions and upon work done at the Bureau of Standards. They are submitted in more detail than might be considered necessary, in order to secure the fullest possible cooperation of other workers in this field in determining the accuracy of reproduction attainable.

Definitions.—The *Clark standard cell* will be understood to mean a voltaic combination having as its positive electrode pure mercury covered with a paste consisting of pure mercurous sulphate mixed with finely divided mercury and pure zinc sulphate crystals and solution, and as its negative electrode an amalgam containing 10 per cent by weight of pure zinc, covered with a layer of pure zinc sulphate crystals, the electrolyte being a solution of pure zinc sulphate in saturation equilibrium with the other constituents of the cell.

The *Weston standard cell* will be understood to mean a similar combination in which the zinc sulphate is replaced throughout by cadmium sulphate and the zinc amalgam by an amalgam containing 12.5 per cent by weight of pure cadmium.

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[1] Kahle: Zs. Instrk. **13**, 191; 1893; Wied. Ann., **51**, 203; 1894.
Jaeger & Wachsmuth: Electrotech. Zs., **15**, 507; 1894; Wied. Ann., **59**, 575; 1896.
Carhart & Hulett: Trans. Am. Electrochem. Soc., **4**, 59; 1904.
Committee Am. Inst. El. Eng., Trans. A. I. E. E., **23**, 827; 1904.
Smith: Electrician (Lond.), **55**, 857; 1905.

It is impossible at present to obtain all the materials employed in the construction of standard cells of sufficient purity for use in *primary* standards, and they should, therefore, be prepared according to the methods described below.

On account of the large electromotive differences found in samples of mercurous sulphate purchased as chemically pure, it is always advisable to subject it to further treatment or to prepare it specially, even when it is intended for use in *secondary* standards. For the latter purpose, C. P. materials may be used without further treatment, unless the zinc and cadmium sulphates are found to be acid to Congo red, in which case they should be recrystallized. Cells set up with ordinary C. P. materials and specially prepared or treated mercurous sulphate should not differ from those in which the most carefully prepared materials are used by more than 0.01 per cent.

PURIFICATION AND PREPARATION OF MATERIALS.

Mercury.—Mercury, as purchased, may contain varying amounts of different metals, such as copper, silver, iron, etc., and by use in the laboratory others, such as zinc, cadmium, and nickel, may be added. If very impure it "tails" when poured from the bottle. In this case it should be first subjected to a preliminary purification by method *a* or *b*.

(*a*) The simplest, though least efficient, method is to shake it for a long time with a solution of mercurous nitrate in dilute nitric acid, or in dilute nitric acid only. Instead of shaking, it may be allowed to fall in very fine drops from a funnel drawn out at the end, through either of the above solutions contained in a long, wide tube, at the lower end of which is sealed a smaller S-shaped tube which serves as a trap. Before introducing the solution some mercury must be poured into the trap, and the first portions that run out must be poured through the funnel again. Instead of one of the above solutions a dilute solution of ferric chloride, slightly acidified with hydrochloric acid, may be used. The treatment must be continued for a long time to completely remove the dissolved impurities, as the action of the solution is necessarily superficial and therefore slow.

(*b*) By making the mercury the anode and a piece of platinum foil the cathode, using 2 per cent nitric acid as the electrolyte, the more positive metals go almost completely into solution by electrol-

ysis, leaving in the mercury the less positive metals which exert only a minor influence on the e. m. f. and which may afterwards be removed, as described under *c* or *d*.

The current density should be about 0.1 amperes per dm², and the electrolysis should be continued, constantly stirring the mercury, for some hours after it no longer tails. The time required depends on the amount and the original condition of the sample. The mercury deposited on the cathode, and possibly containing some of the electropositive impurities, is prevented from dropping back into the anode mercury by suspending under the cathode a small beaker hung from the side of the battery jar by means of a support made of glass rod. The combination anode and stirrer described below may be conveniently used. The depth of the mercury should be great enough to cover completely the blades of the stirrer when rotating, and the volume of dilute acid employed should be at least four times that of the mercury.

Ordinary mercury, or that which has been subjected to either of the preliminary treatments described above, must be further purified by one of the following methods:

(*c*) By double distillation in an ordinary vacuum still.

(*d*) By distillation in a current of air under reduced pressure. For this the form of still described by Hulett and Minchin[2] is recommended.

Zinc and Cadmium.—The traces of impurities ordinarily found in the C. P. metals, purchased from reliable manufacturers, have such a slight influence on the e. m. f. that they may be used without further purification in the preparation of the amalgams for *secondary* standards. For *primary* standards the amalgams may be made by electrolysis, as described below, thus rendering unnecessary the preparation of the pure metals, methods for which are, however, given.

Zinc.—The pure metal may be obtained:

(*a*) By distillation under diminished pressure according to the method of Morse and Burton.[3] A large tube of Jena or Kavalier's combustion glass is closed at one end. The metal is introduced and the tube is then drawn out as close as practicable to the metal. Sev-

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[2] Phys. Rev., **21**, 388; 1905.
[3] Am. Chem. Jour., **10**, 311; 1888.

eral centimeters farther along, according to the amount of zinc used, the tube is again drawn out. As the object of this is to make a reservoir into which the metal is distilled, the tube should not be drawn out symmetrically, but as much to one side as possible, to prevent the melted metal from flowing from one section of the tube to another. The tube is placed in a combustion furnace, connected by means of a rubber stopper and heavy tubing to a mercury or Geryk pump and exhausted. The pump should be kept running not only during the distillation, but afterwards, until the tube has cooled. The tube is first heated at the closed end and by smaller flames under the second section. The flames must be regulated so that the tube does not soften and collapse, and also so that as little zinc as possible is carried over beyond the second section. When about three-fourths of the zinc has distilled off the flames are extinguished and the tube allowed to cool. Air must not be admitted until the metal is perfectly cold. If the tube is sufficiently long, it may be divided into three sections and the zinc distilled from the second into the third, thus effecting a double distillation in practically one operation. The flames under the closed end of the tube should be turned low, but not extinguished, to prevent cooling and consequent cracking. The distilled metal adheres strongly to the glass, which may be removed by hammering with a porcelain pestle.

(*b*) Pure zinc may be obtained by electrolysis of a zinc sulphate solution purified as described below.[4] The 40 per cent solution is electrolyzed, using two platinum cathodes and a pure sheet zinc anode placed between them, but separated by silk partitions. Some zinc oxide is placed around the anode and the solution is continuously neutralized by adding ammonia. In the cell with the cathodes is placed a small platinum anode to keep the solution acid. The metal thus obtained may be distilled or used directly to prepare the amalgam.

Cadmium.—The pure metal may be obtained:

(*a*) By distillation using the same apparatus as described for zinc.[5] It distils at a much lower temperature.

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[4] Mylius and Fromm: Zs. anorg. Chem., **9**, 144 (1895).
[5] Morse and Jones: Am. Chem. Jour., **14**, 261; 1892.

(*b*) By electrolysis of the fused chloride [6] or of a purified solution of the sulphate.[7]

Zinc Sulphate.—The salt is apt to contain sulphates of cadmium, iron, lead, etc., and free sulphuric acid.   The last of these has the greatest effect upon the e. m. f. and promotes the formation of gas in the amalgam limb.   The effect of such small quantities of the other impurities as are apt to be contained in the "chemically pure" salt is practically negligible.   The following methods of purification, both giving the same results in the cell, may be used:

(*a*) Dissolve the pure salt, as purchased, in hot water, add an excess of pure zinc oxide, and keep at nearly the boiling point for several hours to throw down iron as completely as possible.   If the iron is in the ferrous state, its precipitation is greatly hastened by adding pure hydrogen peroxide, a very small quantity of which will suffice to effect its oxidation.   Filter, acidify very slightly with dilute sulphuric acid, and evaporate until the greater part of the zinc sulphate crystallizes out on cooling with ice (5° or lower).   Stir frequently while cooling so as to obtain small crystals.   These are filtered off, using a platinum cone, then washed once or twice with very little ice-cold water, using suction, redissolved in a little hot water, and recrystallized as before.   Further crops of crystals can be obtained from the first and second mother-liquors.   Those from the first are recrystallized once, those from the second mother-liquor twice.   The three lots of crystals are then combined and dissolved in sufficient water to form a saturated solution at room temperature.   The solution is filtered if necessary and set aside to crystallize by spontaneous evaporation in dishes covered with filter paper.   If desired, a saturated solution may be made at not more than 35°, cooled, with constant stirring, by surrounding the beaker with ice, and the crystals filtered off at once.   In the final recrystallization the solution must not be heated at any stage above 35°, on account of the danger of forming a lower hydrate, which takes place at 39°.   In either case the crystals are washed with two or three small portions of ice-cold water, air-dried, and placed in well-stoppered bottles before they begin to effloresce.

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[6] Lorenz: Zs. anorg. Chem., **11**, 49; 1896.
[7] Mylius & Funk: Ibid., **13**, 157; 1897.

The zinc oxide employed is prepared by adding ammonia to a solution of zinc sulphate until the precipitate dissolves. It is then filtered into a large volume of water, allowed to settle, the supernatant liquid decanted and the precipitate thoroughly washed on a Büchner funnel (hardened filter paper), removed from the filter paper and ignited in a platinum crucible inclosed in one of porcelain to prevent access of reducing gases.

(*b*) The zinc sulphate may also be purified by electrolysis.[8] After removal of iron, as described under *a*, a weak current (about 0.1 ampere per dm²) is passed through a solution of zinc sulphate containing suspended zinc oxide to keep it slightly basic. Platinum electrodes are used and the solution is kept stirred. The electrolysis is continued until a clean anode is no longer coated with lead peroxide. The solution is sufficiently pure, though it may still contain traces of other metals. It is filtered, acidified slightly, and the salt recrystallized as described above.

Cadmium Sulphate.—The commercial "chemically pure" salt may contain zinc, lead, ferrous and ferric iron, and occasionally nickel. The salt can be purified by dissolving in an excess of water at about 70°, filtering if necessary, adding an excess of pure cadmium oxide or basic cadmium sulphate and heating for some hours. As much of the iron may be in the ferrous state, a little pure hydrogen peroxide should be added with the cadmium oxide to oxidize the iron. The solution is filtered from precipitated iron and basic cadmium sulphate, acidified slightly, and evaporated nearly at its boiling point in a large porcelain dish resting on a pipestem triangle on a hot plate or supported some distance above the flame of a gas stove or ring burner. Even then the flakes of the lower hydrate of cadmium sulphate which are formed fall to the bottom and cause violent bumping unless they are frequently removed. They are allowed to drain in a funnel with a platinum cone. When the solution has been evaporated to a small volume, it is poured, while still hot, through the funnel, the crystalline flakes are packed down with a pestle, allowed to cool, and washed twice with a little cold water, using suction. They are then redissolved and the solution evaporated down to a small volume as before. After this operation the crystals are dissolved, with mechanical stirring, in an equal weight of water at room temperature, fil-

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[8] Mylius and Fromm: Zs. anorg. Chem., **9**, 144; 1895.

tered if necessary, and set aside in shallow layers (2 to 3 cm) in crystallizing dishes covered with filter paper. Heat should not be employed to hasten the final crystallization on account of the danger of transforming the crystals into a lower hydrate, which takes place at about 70°. If the solution is saturated when placed in the dishes, especially if it be a mother-liquor from which a crop of crystals has been removed, the salt is almost certain to come down in a few hours as a crust over the bottom, instead of isolated crystals. Most of the crystals are cloudy, but those from a purified solution have been found to give as good results in the cells as the perfectly clear ones. The crystals, especially the clear ones, adhere so firmly to the bottom of the dish that they are apt to be broken in removing them. This may be obviated by decanting the mother-liquor and pouring a little pure water over the crystals. In a few moments they will be loosened, without going into solution to any great extent, and may be removed with a spatula. They are to be washed two or three times with water and preserved air-dried in a bottle. Further crops of crystals may be obtained from the mother-liquor, which should first be diluted with about one-tenth its volume of water.

Zinc and Cadmium Sulphate Solutions.—A *saturated* zinc or cadmium sulphate solution is required for making up the paste and for filling the cells. It is prepared by agitating an excess of purified salt with distilled water. In the case of zinc sulphate, shaking with water previously heated to not more than 30° for at least a half hour is sufficient, while for cadmium sulphate mechanical stirring for three or four hours is required on account of the slowness with which it dissolves. In the case of zinc sulphate the mother-liquor, from which a crop of crystals has been removed by cooling, should not be used, as this is unsaturated at room temperature.

Amalgams.—*Zinc amalgam* containing 10 per cent, by weight, of zinc may be prepared by the following methods:

(*a*) By dissolving a weighed amount of pure zinc in 9 times its weight of pure mercury. The latter is heated gently in a porcelain dish on a hot plate or sand bath. The zinc, previously treated with very dilute sulphuric acid to remove the film of oxide, and then washed with water and dried, is placed upon the hot mercury and frequently stirred to hasten solution. The heat is to be increased whenever the amalgam shows a tendency to solidify.

(*b*) A better method, which obviates the preparation of the pure metal, consists in the electrolytic deposition of the zinc from a purified solution of the sulphate, slightly acidified with sulphuric acid, using a weighed amount of mercury as cathode and a rod of the purest commercial zinc as anode. The current strength is measured and the electrolysis continued until somewhat more than the required amount of zinc has been deposited. The amalgam is then removed from the solution, washed thoroughly, dried and weighed, and enough mercury added to bring the amalgam to the required percentage. The anode should be inclosed in filter paper to prevent impurities contained in it from contaminating the amalgam.

Cadmium amalgam, containing 12.5 per cent by weight of cadmium, may be prepared by the same methods as zinc amalgam. On account of its relatively low melting point the temperature of the steam bath is sufficient.

Oxidation of the amalgams.—On exposure to the air the surfaces of the amalgams are slowly tarnished by oxidation. As considerable changes in the composition on the amalgams have no appreciable influence on the electromotive force, this is of no importance. If desired, the oxide may be removed by straining the melted amalgam through a test tube drawn out at the bottom to a small opening, and heated gently to keep the amalgam from solidifying.

Mercurous Sulphate.—The "chemically pure" mercurous sulphate at present obtainable on the market may contain as impurities basic mercurous sulphate, basic mercuric sulphate, traces of nitrate, etc., according to the method of preparation. In addition, the size of grain of the commercial samples, usually prepared by rapid precipitation, may also have an influence on its electromotive properties. Such materials can, therefore, not be employed if the highest accuracy of reproduction is sought. In addition, pure mercurous sulphate hydrolyzes in the presence of water, or even dilute sulphuric acid, so that the washing with water as called for by the old specifications should be omitted. Commercial samples give a higher e. m. f., which decreases for a considerable period after the cell is set up. When, however, mercurous sulphate prepared by one of the following methods is employed, the cells assume their normal values within a few days. As mercurous sulphate is acted upon by light, it should be prepared in a dimly-lighted room and preserved in the dark.

(*a*) The electrolytic method :[9]   Pure mercury, prepared as specified above, is placed in a battery jar of convenient size to a depth of 3 to 4 cm and covered to a depth of 10 to 15 cm with chemically pure 1:6 sulphuric acid.   It is then connected to the negative terminal of a battery or lighting circuit in the usual manner by a platinum wire protected from contact with the solution by a glass tube.   The cathode consists of a small piece of platinum foil immersed in the upper part of the solution. The current is regulated by means of a suitable rheostat to 2 to 5 amperes per dm^2 of exposed anode surface.

To avoid the possible formation of mercuric sulphate, the mercury and the solution should be vigorously and continuously stirred, without, however, breaking up the mercury into small globules. The stirrer may be a glass T-tube with a cross arm of suitable size for the battery jar employed, rotating close to the surface of the mercury.   It may

Fig. 1.

be fastened at the open end of the long arm to a small brass cylinder fitting the sleeve on the shaft of the stirring apparatus.   One end of the cylinder should be turned down so as to fit loosely into the glass tube, to which it is fastened by shellac or hard Khotinsky cement.
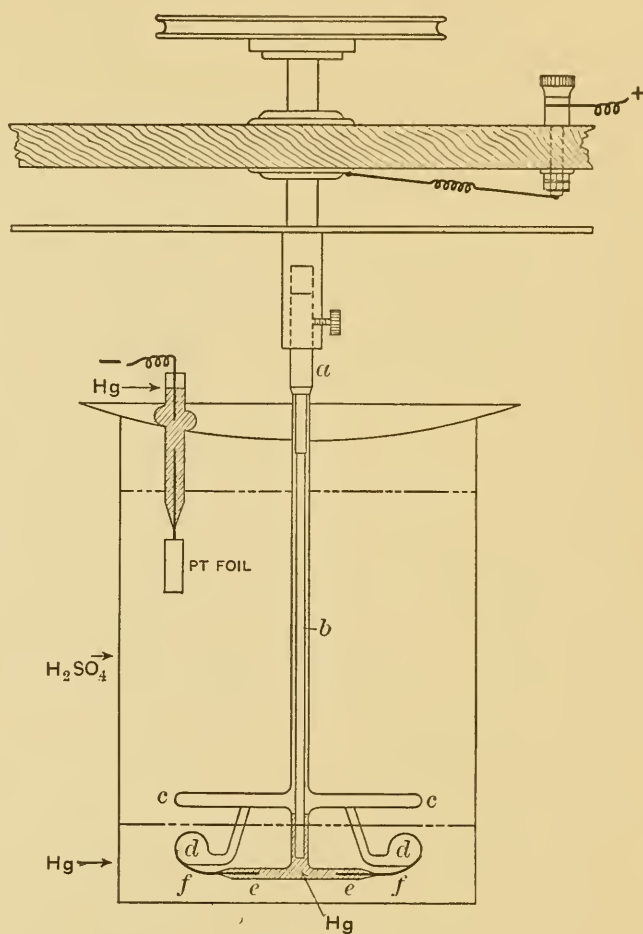
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[9] Carhart and Hulett: Trans. Am. Electrochem. Soc., **5**, 59; 1904. Wolff: Ibid., **5**, 49; 1904.

A still more efficient form of stirrer has a second cross arm about 3 cm above the first, so that both the mercury and the solution in contact with it may be stirred simultaneously.

The most satisfactory form is a combination stirrer and anode connection. The two cross arms, figure 1, *cc* and *ee*, are about 3 cm apart, and the lower arm has short pieces of platinum wire, *ff*, sealed into the ends. The efficiency of the stirrer is increased by the paddles, *dd*, made of glass rod 2 to 2.5 mm in diameter, flattened at the end and sealed to the cross arm, *cc*, and the platinum terminals, thus also making the construction more rigid and preventing the platinum wires from being broken off during cleaning. Contact is made with the bearing of the rotating apparatus by means of a copper wire, *b*, soldered into the lower end of the brass cylinder, *a*, and extending almost to the cross tube, *ee*, the latter and the lower part of the stem being filled with mercury. The soldered joint should be protected from contact with the mercury by a coat of shellac or Khotinsky cement.

The object of this construction is to secure a vigorous stirring of the mercury, so as to continually expose a fresh surface, to prevent the mercurous sulphate formed from heaping up around the usual anode tube and to keep it in suspension. The operation should be watched, as the speed of the stirrer may decrease after the formation of sulphate begins, on account of the greater resistance to be overcome.

The best position of the stirrer can readily be determined by trial, and is that position in which the mercury is vigorously rotated without being broken up into small globules. A speed of 100 to 200 revolutions per minute may usually be employed. The depth of the mercury should be sufficiently great so that the platinum terminals will not be exposed to the action of the electrolyte even during rotation.
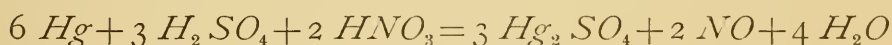
The product formed is light to dark gray, from the presence of finely divided mercury, depending upon the current density, strength of acid, and rate of stirring employed, all of which may be varied between wide limits without appreciably affecting the electromotive properties of the product. To minimize the possible influence of size of grain the stirring is preferably continued for some hours after the current is interrupted.

The mercurous sulphate, separated from the excess of mercury, which interferes with its subsequent washing, by means of a separating funnel (using no grease on the stopcock) or by means of a pipette, should then be transferred to a clean glass-stopped bottle and preserved in the dark under 1:6 sulphuric acid.

The theoretical rate of formation is 5 grams per ampere hour. Where a considerable quantity is formed, sufficient sulphuric acid may be added from time to time to make up for that which has combined with the mercury, or 1:5 sulphuric acid may be used in place of that specified above.

(*b*) Mercurous nitrate is prepared by the action of strong, C. P. nitric acid on an excess of pure mercury and the concentrated solution diluted with five volumes of distilled water, adding, if necessary, a few drops of nitric acid to clear up any cloudiness due to the formation of basic nitrate. This solution is then added drop by drop, with constant stirring, to 5 volumes of 1:4 sulphuric acid. Wash several times by decantation with 1:6 sulphuric acid and preserve in the dark in a glass-stopped bottle with mercury and acid of the same strength.

(*c*) A simpler method, in which the preparation of mercurous nitrate is avoided, consists in the treatment of mercury with sulphuric acid containing a small percentage of nitric acid. The reaction which takes place is that involved in the Lunge method for the estimation of nitrates, so that practically all the nitric acid is eliminated from the solution.

$$6\,Hg + 3\,H_2SO_4 + 2\,HNO_3 = 3\,Hg_2SO_4 + 2\,NO + 4\,H_2O$$

The rate of the reaction depends on the concentration of the sulphuric acid, the amount of nitric acid present, and the temperature. The mercury, covered with a liter of hot 1:2 sulphuric acid, is contained in a beaker on a hot plate. Five cc concentrated nitric acid are then added and the whole stirred vigorously for some time after the reaction is completed, as shown by the disappearance of the brown fumes of nitrogen peroxide. On account of these fumes a well-ventilated hood is desirable. The product formed, which is quite gray from the presence of finely divided mercury, is washed several times by decantation with 1:6 sulphuric acid and preserved in the dark in a glass-stopped bottle with acid of the same strength.

(*d*) By reduction of mercuric sulphate with mercury. Twenty-five grams of mercury are added to 50 cc boiling concentrated sulphuric acid in a porcelain dish, continuing the heating for some time after all the mercury has dissolved. Cool, pour in 500 cc of 1:6 sulphuric acid, and add the diluted solution, drop by drop, to a liter of the same acid contained in a large beaker with a 2 cm layer of mercury, vigorously stirring both the solution and the mercury. The stirring should be continued for some hours after all the mercuric sulphate has been added   The dark-gray product is washed and preserved as under (*c*).

(*e*) By recrystallization of commercial mercurous sulphate.[10] Fifty grams of commercial mercurous sulphate and 25 grams of mercury are added to 200 cc concentrated sulphuric acid previously heated to 150°. Stir about ten minutes, allow to settle if necessary, and pour slowly and with constant stirring into about 10 volumes of 1:6 sulphuric acid. To avoid spattering, the beaker containing the dilute acid is covered with a perforated watch glass, and the hot solution is introduced through a narrow-stemmed funnel extending almost to the surface of the acid.

(*f*) Ordinary commercial samples, differing widely in their electromotive properties from samples prepared by the preceding methods, may be brought into sufficiently close agreement for use in secondary standards by digestion with hot dilute sulphuric acid. Fifty grams of the salt are finely ground, preferably in an agate mortar, with enough 1:4 sulphuric acid to make a thin paste. This is poured into a beaker containing 250 cc of 1:4 acid, the finer particles being separated by decantation. The coarser particles are to be retreated in the same way three or four times, regrinding if necessary. After adding 20 cc of mercury, the whole is heated for three hours to 100°, with vigorous stirring, which should be continued until the acid has cooled. The stirring may be interrupted from time to time to wash down any particles of mercurous sulphate which may collect on the sides of the beaker above the level of the liquid and therefore become exposed to the combined action of water condensing on the walls and oxygen from the air.

The Paste.—This should be freshly prepared before setting up the cells. It is obvious from the irregular, pitted character of the

[10] Smith: Electrician (London), **55**, 857; 1905.

mercurous sulphate crystals, as shown under the microscope, that the greatest care must be taken in washing the sample to completely remove all traces of acid.

This is most easily done in a Gooch crucible of about 25 cc capacity with a disk of hardened filter paper at the bottom. The disks are cut to size with a cork-borer, warmed for some time with dilute nitric acid, washed with hot distilled water until acid-free, and dried. A sufficient quantity of the sulphate, shaken up with the acid under which it is preserved, is poured into the crucible, care being taken not to transfer any mercury, which interferes with the washing, the acid removed by suction, and the salt washed twice with small portions of 1:6 sulphuric acid to remove possible traces of mercuric sulphate formed by the action of air in the bottle. The acid is removed by washing with five or six small portions of redistilled absolute alcohol, care being taken to wash down the sides of the crucible. To completely remove the alcohol the sulphate is then washed three or four times with a saturated solution of $\left\{ \begin{array}{l} \text{zinc} \\ \text{cadmium} \end{array} \right\}$ sulphate, taking the same precautions as with the alcohol. If the alcohol is not available, two or three additional washings with the sulphate solution will suffice. If the paste cracks or separates from the sides of the crucible, more of the wash liquid is to be added and the contents of the crucible thoroughly stirred up before again applying suction. After scraping off the upper layer, the mercurous sulphate is transferred to a small, clean, dry beaker or crucible, mixed with one-third to one-half its volume of finely powdered $\left\{ \begin{array}{l} \text{zinc} \\ \text{cadmium} \end{array} \right\}$ sulphate crystals and sufficient saturated $\left\{ \begin{array}{l} \text{zinc} \\ \text{cadmium} \end{array} \right\}$ sulphate solution to make a moderately thin paste. A large excess of $\left\{ \begin{array}{l} \text{zinc} \\ \text{cadmium} \end{array} \right\}$ sulphate crystals in the paste should be avoided so that practically every part of surface of the mercury electrode will be in contact with mercurous sulphate, thus securing a rapid attainment of saturation equilibrium. With white samples of mercurous sulphate one-third their volume of mercury should be added in making up the paste. To eliminate possible influence of size of grain, the mercurous sulphate should not be ground, and the paste should be stirred as little as possible in its preparation.

The Cells.—For facility in filling and sealing the H type is recommended. The size and dimensions, although not affecting the e. m. f., determine the polarization produced by the passage of a current and the rapidity with which the cell assumes the temperature of its surroundings. Figure 2, drawn to half scale, gives the dimensions of the cells made at the Bureau, and which have been found entirely satisfactory. Especial care must be taken in sealing in the platinum wires (B. & S. No. 32) and subsequent annealing. As recommended by Hulett, the platinum wire inside the cell may be covered with a thin layer of glass to within 1 mm or less from the end.

Clark cells frequently crack at the point where the platinum terminal is sealed into the amalgam limb. This may be avoided by a
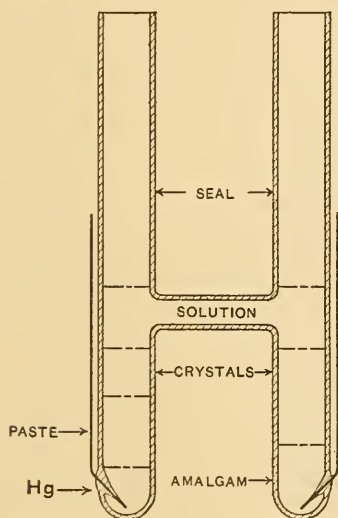

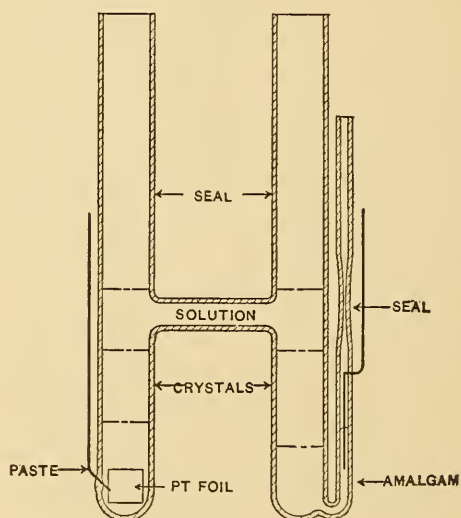Fig. 2.   Fig. 3.

construction recommended by Kahle and shown in figure 3, in which the platinum terminal of the amalgam limb is sealed into a side tube, contact being made by sucking the amalgam up into this tube while it is still liquid. The platinum wire should extend downward about 2 cm below the point at which it is sealed into the tube and the amalgam should cover only its lower half, thus preventing the glass from cracking at the seal. This construction also reduces the chance of contact between the platinum and the electrolyte and for this reason is preferable for portable cells.

As the cells are to be sealed off above the cross arm after filling, they may be slightly constricted beforehand, but if the wall thick-

ness is not greater than 0.75 mm this will not be found necessary. The length of the tube above the cross-arm as shown in figures 2 and 3, although greater than absolutely necessary, facilitates the sealing but at the same time somewhat increases the difficulty of filling.

Cleaning the cell.—If the cells and filling tubes are badly contaminated with grease, etc., they should be covered with chromic acid mixture and allowed to stand over night. Too long a contact of the cells with this cleaning mixture should be avoided on account of the danger of forming lead chromate from the lead sealing-in glass employed. The cells should then be washed with distilled water, filled with aqua regia, which is allowed to remain in them for thirty minutes, and repeatedly washed with distilled water. The action of the aqua regia on the platinum wires facilitates subsequent amalgamation. Ordinarily the cleaning with chromic acid mixture may be omitted.

Amalgamation of the platinum terminals.—In order to minimize the possibility of contact between the electrolyte and the platinum terminals, especially from shaking in transport, they should be amalgamated with a solution of pure mercurous nitrate in dilute nitric acid. The amalgamating solution is introduced into the cell and a weak current is passed through it from a platinum wire anode to the platinum terminal externally connected to the negative pole of a battery. Sufficient mercury is deposited in a short time.

For portable cells the limb intended to receive the paste may be provided with a platinum foil electrode welded to the platinum wire. (Fig. 3.) In this case the whole surface must be thoroughly amalgamated, for which a proportionately longer time is required. Especial care must be taken, as the amalgamated foil is employed to replace the mercury.

To remove every trace of the amalgamating solution the cell is next washed several times with dilute nitric acid and finally repeatedly rinsed with distilled water. The amalgamated surface may be "rinsed" with a small quantity of pure mercury and the cell then dried in an air bath at 110°.

Introduction of the materials.—The materials are most easily and neatly introduced by means of filling tubes. Great care should be taken not to allow them to come in contact with the walls of the cell.

The amalgam.—The zinc or cadmium amalgam, prepared as

described above, is heated slightly above its melting point and a quantity of it sufficient to cover the platinum terminal to a depth of at least 10 mm is transferred to the cell by means of a previously heated, clean, dry pipette. A pipette with a rounded end, at the center of which is a small hole, will be found more satisfactory than one drawn out to a capillary, which the amalgam tends to clog up owing to cooling. After heating the pipette, which is provided at the upper end with a rubber tube, it is introduced below the surface of the amalgam, meanwhile blowing through it to avoid the introduction of any of the film of oxide on the surface. A suitable amount of amalgam is then drawn into the pipette by gentle suction, the suction being released while the pipette is removed from the amalgam, and then applied again sufficiently to prevent any more of the amalgam from running out. Any particles of the amalgam adhering to the outside are then removed by wiping with filter paper and the pipette quickly introduced into the cell to within 2 cm of the bottom. On releasing the suction the amalgam will run out freely, the amount introduced being regulated by again applying suction at the proper moment. The pipette is then withdrawn without touching the walls of the cell, which, if necessary, may be protected by means of a thin glass tube of slightly less diameter than the cell. The amalgam may also be introduced by means of a narrow-necked funnel previously heated.

Particles of amalgam on the cell wall can not exert any influence on the e. m. f. except when forming an integral part of the amalgam electrode and not fully covered with crystals. They can be removed by the aid of a glass rod, but great care must be taken to prevent them from reaching the other limb and contaminating the mercury, which would of course seriously influence the e. m. f.

Introduction of the mercury.—The mercury may be introduced into the cell in a similar manner. If a pipette be used it must, however, be drawn out to a *very* fine capillary. The simplest method consists in pouring into the cell sufficient mercury to cover the platinum terminal to a depth of at least 10 mm, care being taken not to introduce any into the amalgam limb. By cautious tilting air bubbles entrapped under the mercury can easily be removed.

Introduction of the paste.—The paste, prepared immediately before setting up the cell, as described above, is most neatly introduced by means of a pipette with an opening 3 to 4 mm in diameter. Its consistency should be such that it can be readily drawn up into and flow from the pipette; and, therefore, finely-crushed $\begin{Bmatrix} \text{zinc} \\ \text{cadmium} \end{Bmatrix}$ sulphate crystals should be employed. After filling the carefully cleaned and dry pipette with paste, it should be wiped with clean filter paper, and a small amount of the paste allowed to flow out. The end of the pipette is then brought close to the mercury and paste allowed to flow into the limb to a depth of 1.5 to 2 cm, care being taken to keep the cell walls clean and to avoid trapping air bubbles.

The paste may also be introduced by means of a thistle tube extending to within 2 cm of the surface of the mercury. If necessary the walls of the cell may in addition be protected by a guard tube.

Introduction of the crystals and solution.—The amalgam and paste are next covered to a depth of about 1 cm with *saturated* $\begin{Bmatrix} \text{zinc} \\ \text{cadmium} \end{Bmatrix}$ sulphate solution, after which pulverized $\begin{Bmatrix} \text{zinc} \\ \text{cadmium} \end{Bmatrix}$ sulphate is introduced, a little at a time to avoid trapping air bubbles, to a depth of 1.5 to 2 cm by means of a wide-stemmed funnel. The cell is then filled slightly above the cross arm with *saturated* $\begin{Bmatrix} \text{zinc} \\ \text{cadmium} \end{Bmatrix}$ sulphate solution.

In order to maintain a concentration equilibrium at all temperatures to which the cell is likely to be exposed, in all cases a saturated solution of zinc or cadmium sulphate and a sufficient excess of the corresponding crystals over the amalgam and in the paste should be employed. The layer of crystals in the mercury limb is intended as a further precaution against their leaching out of the paste, as sometimes happens when the solution is not completely saturated.

Sealing.—The cell is now sealed by the aid of two small horizontal blowpipe flames applied to the cell wall from opposite directions. One limb of the cell is closed by a cork and the other by a cork nicked at one side, through which passes a glass rod to serve as a

handle in drawing it out. The cell is gradually heated 2 to 3 cm above the level of the liquid until the danger of cracking has passed, and then held in the flame, rotating meanwhile, until the tube almost collapses, after which it is closed by drawing it out slowly. By judicious heating the seal may be nicely rounded by the expansion of the enclosed air. The second limb is sealed in a similar manner.

Whenever, in filling the cell, the materials accidentally come in contact with the part of the glass which is to be heated in sealing, it is first cleaned by wiping with filter paper slightly moistened with distilled water and then with dry paper.